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Low Temperature Curing of a Nitrile-Epoxy Adhesive

By J. S. Tira

Published April 1981

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Final Report

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NITRILE-EPOXY ADHESIVE

By J. S. Tira

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Final Report
J. S. Tira, Project Leader

Project Team:
J. C. Harbord

Technical Communications



**Kansas City
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Adhesive strength and glass transition temperature were correlated with cure times at 85°C and above. The effect of moisture on adhesive cure and strength was tested. With a 3-hour cure at 85°C, lap shear strength met specification requirements. The adhesive was found to absorb moisture with time, especially if one or both polyethylene covers are removed. Placing the adhesive in a desiccator for 30 minutes produced excellent room temperature shear strengths. Preconditioning (removal of moisture) is critical for elevated temperature cures.

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SUMMARY

The engineering design of a Bendix Kansas City produced electronic assembly requires the use of an adhesive to attach various electrical components to a metallic baseplate. This study used the nitrile-epoxy film adhesive FM-123-5. Its strength and glass transition temperature (T_g) were correlated with cure times at 85°C and above. Lap shear strength values met room temperature requirements with a 3-hour cure at 85°C. However, to obtain a fully cured adhesive with a T_g of $\geq 90^\circ\text{C}$, an 8-hour cure is recommended. A summary of T_g for different cure times at 85°C is reported.

The effects of moisture on the adhesive were tested. The adhesive was found to absorb moisture with time, especially if one or both of the polyethylene covers are removed. These covers should remain on the adhesive until the material is ready to use or until the adhesive is placed in a desiccator. Adhesive preconditioned in a desiccator for 30 minutes produced excellent room temperature lap shear strengths using 85, 93, and 116°C cure temperatures. Preconditioning (removal of moisture) is critical for elevated temperature cures.

The adhesion, or T-Peel strength, is reduced by using an 85°C cure with 0.07 MPa pressure rather than the optimum 116°C cure with 0.21 MPa pressure. Using flowing dry nitrogen gas over the uncovered adhesive surface is not recommended because it dries the adhesive, thus reducing the flow during adhesive cure. To verify the degree of cure, a small sample of the cured adhesive should be analyzed with a thermal mechanical analyzer (TMA) to determine the T_g .

DISCUSSION

SCOPE AND PURPOSE

Previous electronic assembly designs attached various electrical components to a metallic baseplate mechanically. This design calls for the use of an adhesive to attach electrical components. This bonding adhesive must be cured at a low ($<100^{\circ}\text{C}$) temperature because some electrical components are sensitive to temperature.

The film adhesive FM-123-5 from American Cyanamid was selected for this application. The advantage of the film is that it provides uniform bond thickness, which is critical because of maximum height restrictions on the components. Additionally, this modified nitrile-epoxy has good adhesion (peel strength) that meets Federal Specification MMM-A-132, Type 1, Class 2 (Heat Resistant Airframe Structural Adhesives, Metal-to-Metal).

Good adhesion is important because the assembly is subjected to g-load, shock, and vibration. Therefore, the cure of the adhesive as it relates to strength was tested. Concurrently, the effect of moisture upon the cure and strength of the adhesive was evaluated.

ACTIVITY

Adhesive Material Description

FM-123-5 is a supported film adhesive manufactured by the Bloomingdale Department of American Cyanamid. The adhesive is described as a modified nitrile-epoxy adhesive supplied on a knitted monofilament nylon carrier.¹ It is designed for structural bonding of both sandwich and metal constructions and has a serviceable range from -57 to $+121^{\circ}\text{C}$. The material used is nominally 0.2 mm thick. The hardener used with the nitrile-epoxy is dicyandiamide, a nonresinous amide-amine. The material is a solid powder dispersed in the resin and calendered on the nylon carrier. When the adhesive is heated, the dicyandiamide breaks down and cures the nitrile-epoxy resin.

Effect of Cure Time on Lap Shear Strength and Tg

The lowest possible cure temperature is desirable to protect electrical components that are sensitive to temperature. A series of tensile lap shear specimens was prepared using the lowest recommended cure temperature (85°C) at various cure times. Test specimens were prepared according to ASTM-D-1002, except that the aluminum test specimens were glass-bead blasted and vapor degreased instead of acid etched.

Four lots of adhesive were tested. The test specimens were shimmed to produce a 0.127-mm bondline thickness. All specimens were placed in a room temperature oven and heated to the cure temperature of 85°C. The cure cycle was timed after a 1-hour heatup. Table 1 is a summary of the lap shear strength results. Figure 1 presents the same data graphically, illustrating that the lap shear strength increases with cure time at 85°C. A minimum cure time of 8 hours at 85°C appears necessary to obtain maximum and repeatable shear strength.

Concurrent with curing the mechanical test specimens, additional samples of the adhesive were cured in the same oven at the same time on Teflon-coated fabric. These samples were later analyzed on a thermal mechanical analyzer (TMA) to determine the glass transition temperature (T_g) of the cured adhesive. The T_g indicates the degree of cure of the material. The manufacturer has indicated that the T_g for completely cured adhesive is approximately 100°C. Figure 2 is a plot of the T_g of five lots of the FM-123-5 adhesive after cure at 85°C for varying times. A minimum cure time of 8 hours appears necessary to obtain a T_g above 90°C.

Component bonding is a multistep operation. Some electrical components are bonded before others, although all are bonded at 85°C. Although the data in Figure 1 indicate that a high strength bond can be achieved with only a 3-hour cure cycle at 85°C, the data presented in Figure 2 indicate the adhesive is not necessarily cured. A second bonding operation at 85°C could soften the first adhesive bond as the second cure cycle progresses through the T_g of the undercured adhesive. Above the T_g the adhesive is soft and pliable which can permit parts to move or even come unbonded.

Weight Change of Adhesive Stored in Different Environments

Samples of film adhesive approximately 50.8 by 50.8 mm were placed in containers with controlled environments to determine how they would respond upon removal from refrigerated storage. The polyethylene cover was removed from one surface of each sample. Three environmental storage conditions were used: 90 and 50 percent relative humidity (RH) and flowing dry nitrogen gas. The samples were periodically removed from their controlled environment, immediately weighed, and returned.

Table 2 is a summary of the weight change data. As noted in the table, the 0.41 percent weight increase in 2 hours in a 90 percent RH indicates that the samples absorb moisture quickly. Some of the increase in weight is probably due to absorption of moisture by the knitted nylon carrier.

Two sets of data are presented for the adhesive film samples stored in the flowing dry nitrogen gas. The reason for the difference in data is attributed to the variance in weight of the adhesive film samples, although their dimensions were essentially

Table 1. Room Temperature Lap Shear Strength (MPa) of Adhesive Cure at 85°C

Lot Number								
Cure Time (h)	1178		1240		1231		1261	
	\bar{X}	S	\bar{X}	S	\bar{X}	S	\bar{X}	S
1	3.7	1.0					6.2	0.2
2	18.4	0.3	2.9	0.8			21.7	0.7
3	22.5	0.4	17.7	2.8	17.9	2.4		
4	21.7	1.0						
5	22.3	0.1	23.1	0.8	21.9	0.5		
7	21.8	1.4	23.2	2.4	16.8	2.4	19.3	0.8
15	25.8	0.8	19.8	2.5	25.0	2.2	19.5	1.1

\bar{X} = Median, average of 5 test specimens per cure condition.
S = Standard Deviation.

identical. The heavier weight samples stored in the nitrogen environment had the lower weight losses. A possible explanation may be that the moisture in the nylon carrier has more difficulty permeating the thicker adhesive layer. A second possibility is that the heavier adhesive samples may contain a smaller quantity of butyl glycidyl ether, a reactive diluent. This may explain why one set of samples has more adhesive than another. In any case, the film adhesive is capable of absorbing moisture. It also will lose weight (possibly reactive diluent) in a flowing dry nitrogen environment.

Effect of Preconditioning on Adhesion (T-Peel Strength)

FM-123-5 adhesive film is stored at subambient temperature to prolong its usefulness. The adhesive may be removed from refrigerated storage numerous times. Before it is used, the adhesive must be taken out of storage and allowed to warm to room temperature. During this time, moisture may condense on the film. The effects of moisture on adhesive strength and Tg are unknown, as are the effects of a low temperature cure upon adhesion.

A series of 11 test sets of T-Peel specimens were prepared, each with different adhesive preconditioning. The first set of specimens was prepared according to the manufacturer's recommended cure

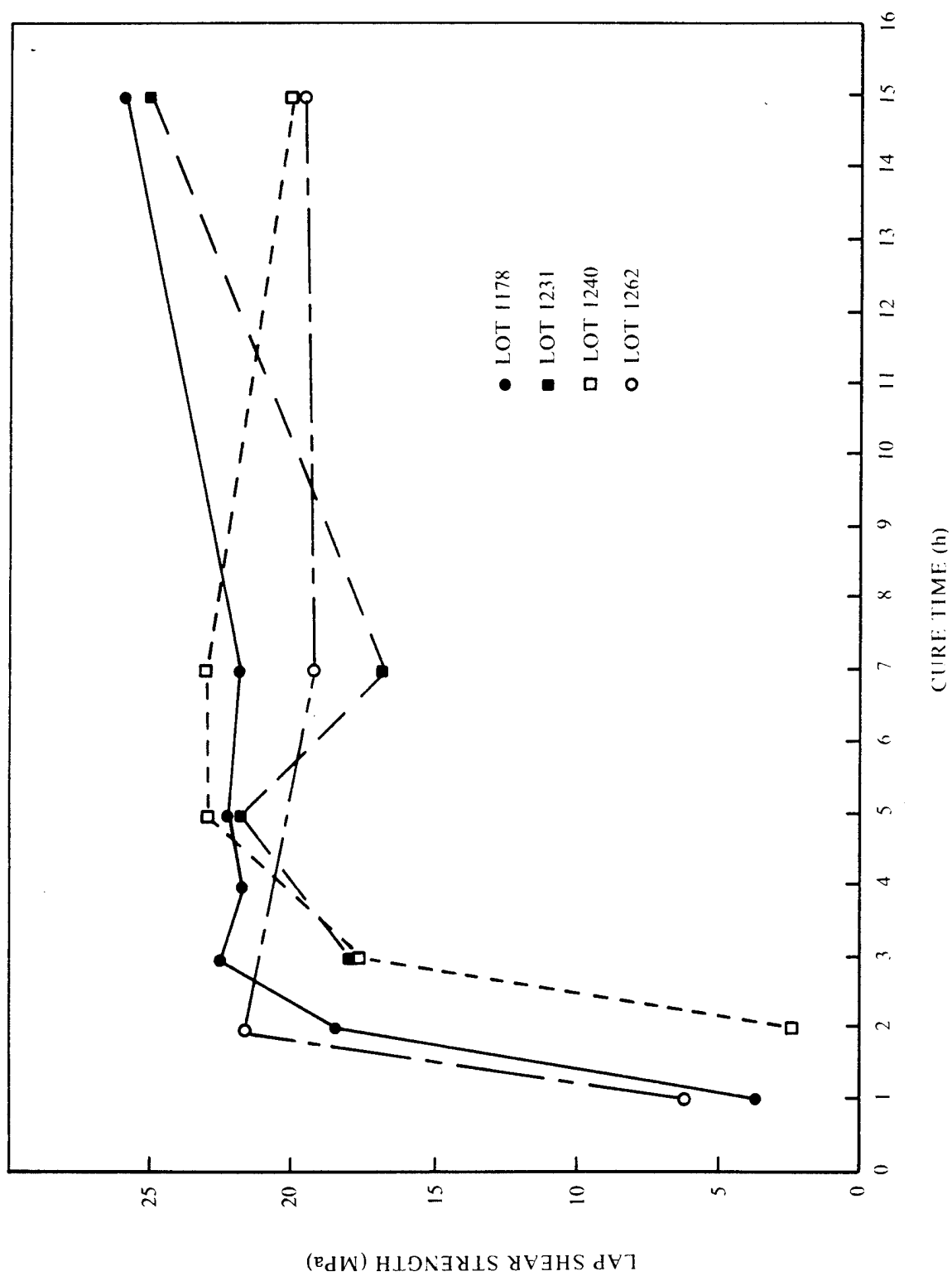


Figure 1. Lap Shear Strength Versus Cure Time at 85°C

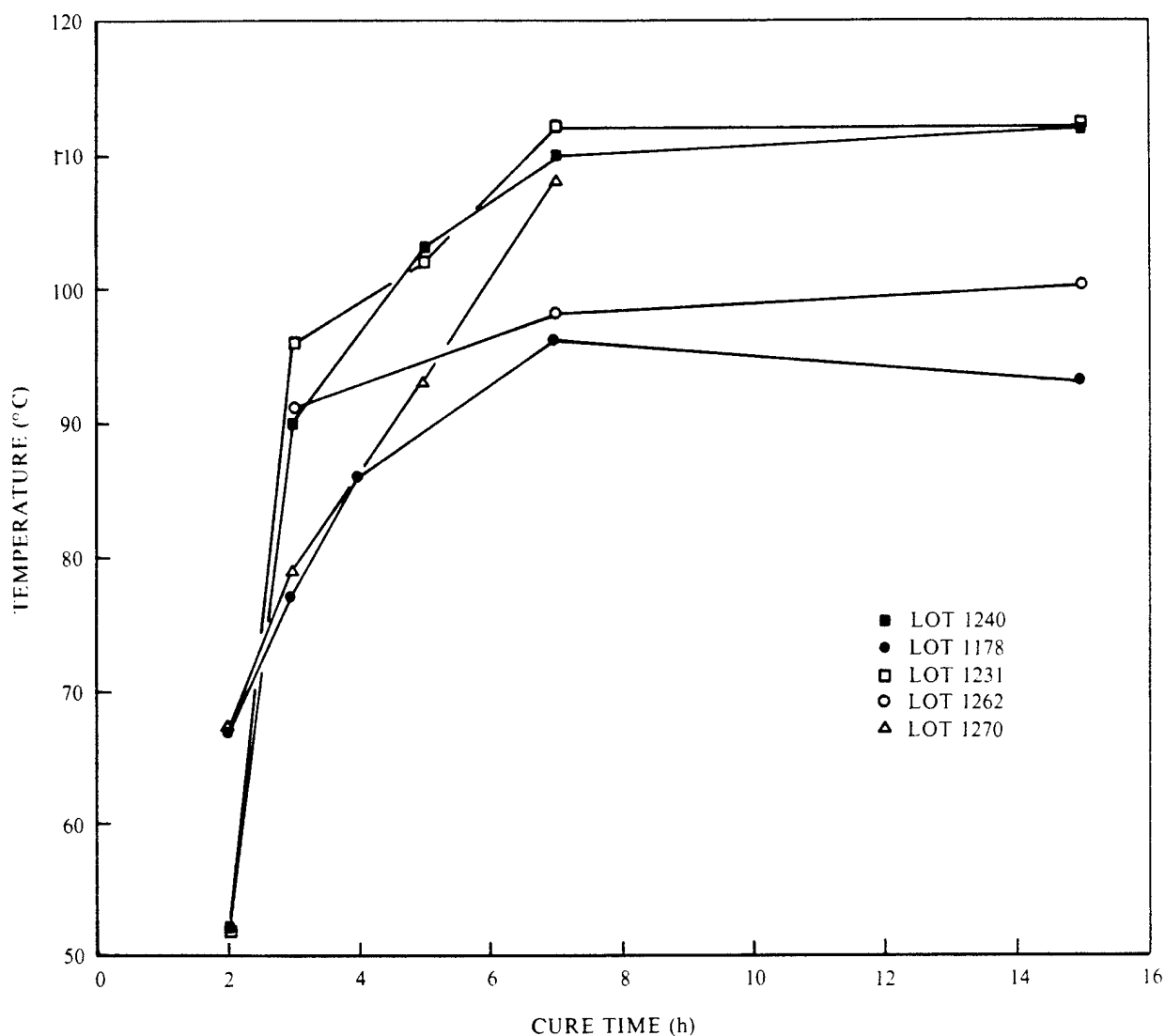


Figure 2. Tg Versus Cure Time at 85°C

schedule--116°C for 3 hours with 0.21 MPa pressure. A second set of specimens was prepared at an intermediate cure temperature of 93°C. Some were cured for 3 hours and some for 7 hours with 0.07 MPa pressure. Most test specimens were prepared according to a cure schedule used in production--85°C for 7 hours at 0.07 MPa pressure. Specimens were prepared with aluminum adherends treated according to ASTM-D-2651-69, Method A (Preparation of Metal Surfaces for Adhesive Bonding). The T-Peel test specimens were prepared and tested according to ASTM-D-1876-72 (Peel Resistance of Adhesives). Each preconditioning and cure

Table 2. Weight Change (Percent) of Film Adhesive

Time in Controlled Environment (h)	Storage Atmosphere		
	Rh (Percent)*		Flowing Dry Nitrogen Gas** (Percent)
	90	50	
2	+0.41	+0.21	-0.28, -0.07
4	+0.61	+0.30	-0.58, -0.15
7	+0.83	+0.41	-0.46, -0.19
24	+1.7	+0.76	-0.65, -9.41
28	+1.8	+0.73	-0.68, -0.40
48	+2.0	+0.83	-0.80, -0.46
72	+2.2	+0.84	-0.97, -0.70
96	+2.4	+0.95	-0.97, -0.70
168	+2.4	---	-1.03, ---

*Average of four test specimens.

**Average of two test specimens.

cycle underwent five tests. Table 3 is a summary of the test specimen matrix and the results. These conclusions were reached.

1. The manufacturer's recommended cure schedule of 116°C for 3 hours and 0.21 MPa pressure produces the highest adhesion (T-Peel strength) results.
2. Lower cure temperatures with lower bonding pressures reduce adhesion.
3. Increased cure time at the lower cure temperatures (93° and 85°C) does not affect adhesion, although it increases Tg. (Data reported in Table 1 show that lap shear strength is not appreciably improved with a longer cure time--3 hours versus 7 hours--for an 85°C cure; however, there is a considerable variance in the data from lot to lot.)
4. Excessive drying of the adhesive film in flowing dry nitrogen gas reduces the adhesion, probably because any residual solvent or diluent is removed, which reduces flow during cure. However, Tg is increased, probably because the last traces of moisture are removed.

Table 3. Adhesion (T-Peel Strength) of Film Adhesive

Adhesive Preconditioning	Cure			Adhesion Median* (kg/25.4 mm)
	Temperature (°C)	Pressure (MPa)	Time Tg (h) (°C)	
Bonded Immediately After Removal From Freezer	116	0.21	3 104	14.8
50 Percent RH for 4 h	116	0.21	3 110	9.0
Bonded Immediately	93	0.07	3 100	7.8
Bonded Immediately	85	0.07	3 86	4.7
Bonded Immediately	85	0.07	7 96	5.1
Flowing N ₂ Atmosphere				
For 4 h	85	0.07	7 96	3.1
For 24 h	85	0.07	7 96	1.7
For 48 h	85	0.07	7 100	1.5
90 Percent RH for 4 h	85	0.07	7 98	4.5
50 Percent RH for 4 h	85	0.07	7 105	8.3
50 Percent RH for 24 h	85	0.07	7 96	4.0

*Average of 5 test specimens.

5. Adhesive storage in a high humidity (~90 percent) or long term storage (~24 hours) in a moderate humidity (~50 percent) does not significantly reduce the room temperature adhesion or Tg of the FM-123-5 adhesive for low temperature (85°C) cure.

However, test samples preconditioned in 50 percent RH for 4 hours and then cured according to the manufacturer's recommendation had adhesion values almost 30 percent lower than samples made with adhesive removed from the freezer and immediately bonded. Therefore, absorbed moisture may be critical to adhesion for adhesive cured at temperatures over 100°C. The bar chart in Figure 3 shows the effect of a preconditioning environment on adhesion (T-Peel strength).

Effect of Preconditioning on Room Temperature Lap Shear Strength

Two sets of lap shear specimens were prepared from the same lot of FM-123-5 adhesive. One set of adhesive was stored at the normal storage temperature of -29°C and was then placed in a desiccator for 30 minutes before bonding. The other set of adhesive was stored in the freezer at -29°C for 2 to 3 days with the cover sheet removed from one surface. Upon removal from the freezer the adhesive was allowed to warm to room temperature. During that time, frost condensed on it.

Lap shear test specimens were prepared and cured at 85, 93, and 116°C for 8 hours. Test results are compared in Figure 4. Adhesive which had been conditioned in a desiccator for 30 minutes produced the consistently higher lap shear strength, regardless of cure temperature. Adhesive which had been unprotected in the freezer produced the lower lap shear strength, especially at the lower cure temperatures of 85 and 93°C. Lap shear strengths for both adhesives were the same at a cure temperature of 116°C. Therefore, the adhesive should be placed in a desiccator for approximately 30 minutes before bonding, regardless of the anticipated cure temperature.

Effect of Preconditioning on Elevated Temperature Lap Shear Strength

Lap shear test specimens were prepared and tested to evaluate the effects of adhesive preconditioning on the elevated temperature strength of the FM-123-5 adhesive film. Two sets of test specimens were made with the same lot of adhesive. One preconditioning cycle involved exposure to flowing dry nitrogen for 4 hours. The other preconditioning involved exposure to a 90 percent RH for 4 hours. All specimens were bonded at the recommended cure cycle of 116°C for 3 hours at 0.21 MPa bonding pressure.

The test data are reported in Figure 5. The adhesive preconditioned in the flowing dry nitrogen exhibited a superior shear

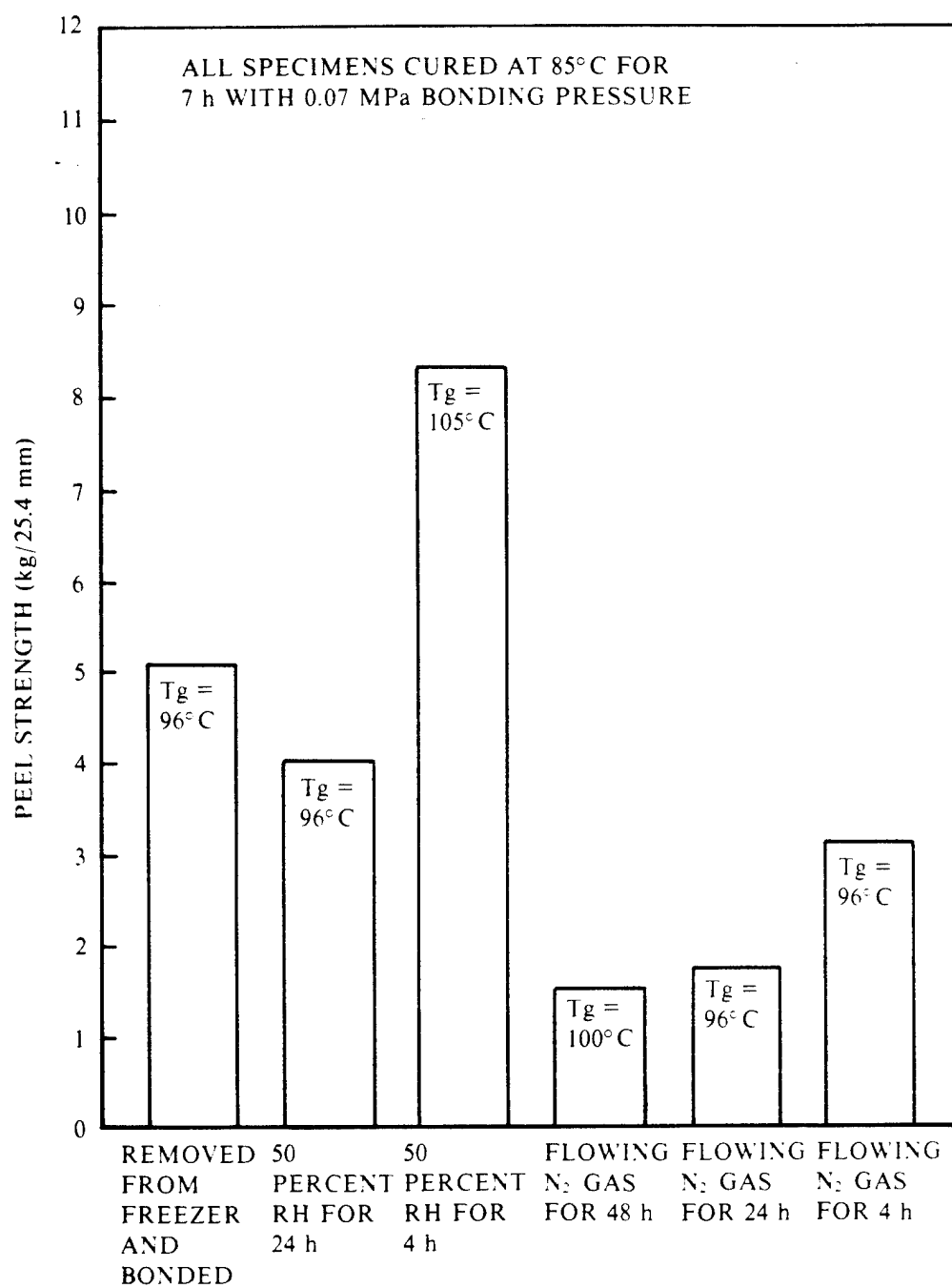


Figure 3. Effect of Adhesive Preconditioning on Adhesion (T-Peel Strength)

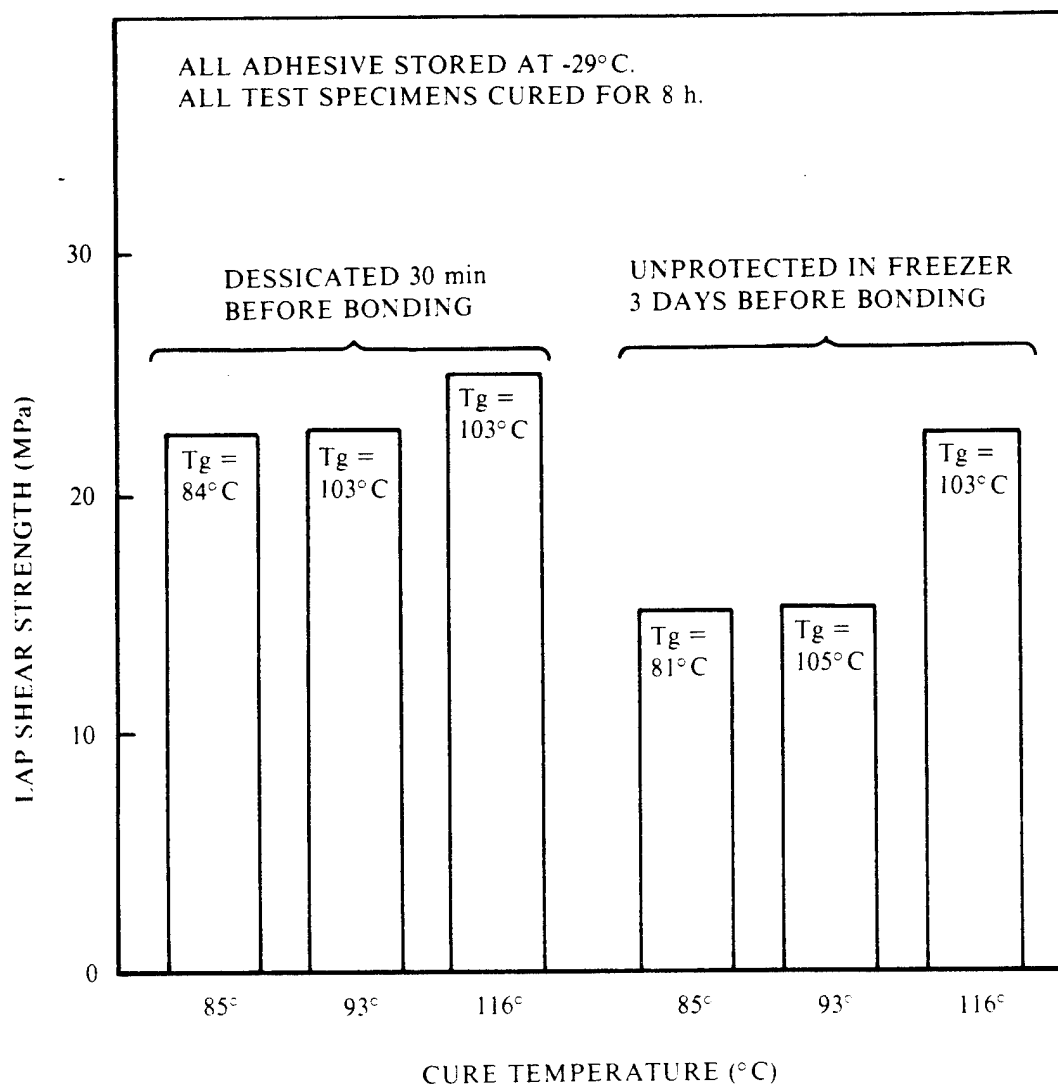


Figure 4. Room Temperature Lap Shear Strength

strength at all three test temperatures (25°C, 82°C, and 121°C). As the two adhesives reached 121°C, their shear strengths were essentially identical. No further testing was performed.

Outgassing Study of Uncured Adhesive

The direct probe mass spectrometer was used to investigate the outgassing of uncured adhesive from ambient temperature to 120°C. The pressure during this analysis ranged from 1×10^{-6} to 2×10^{-6} mm of Hg. Results are shown in Table 4.

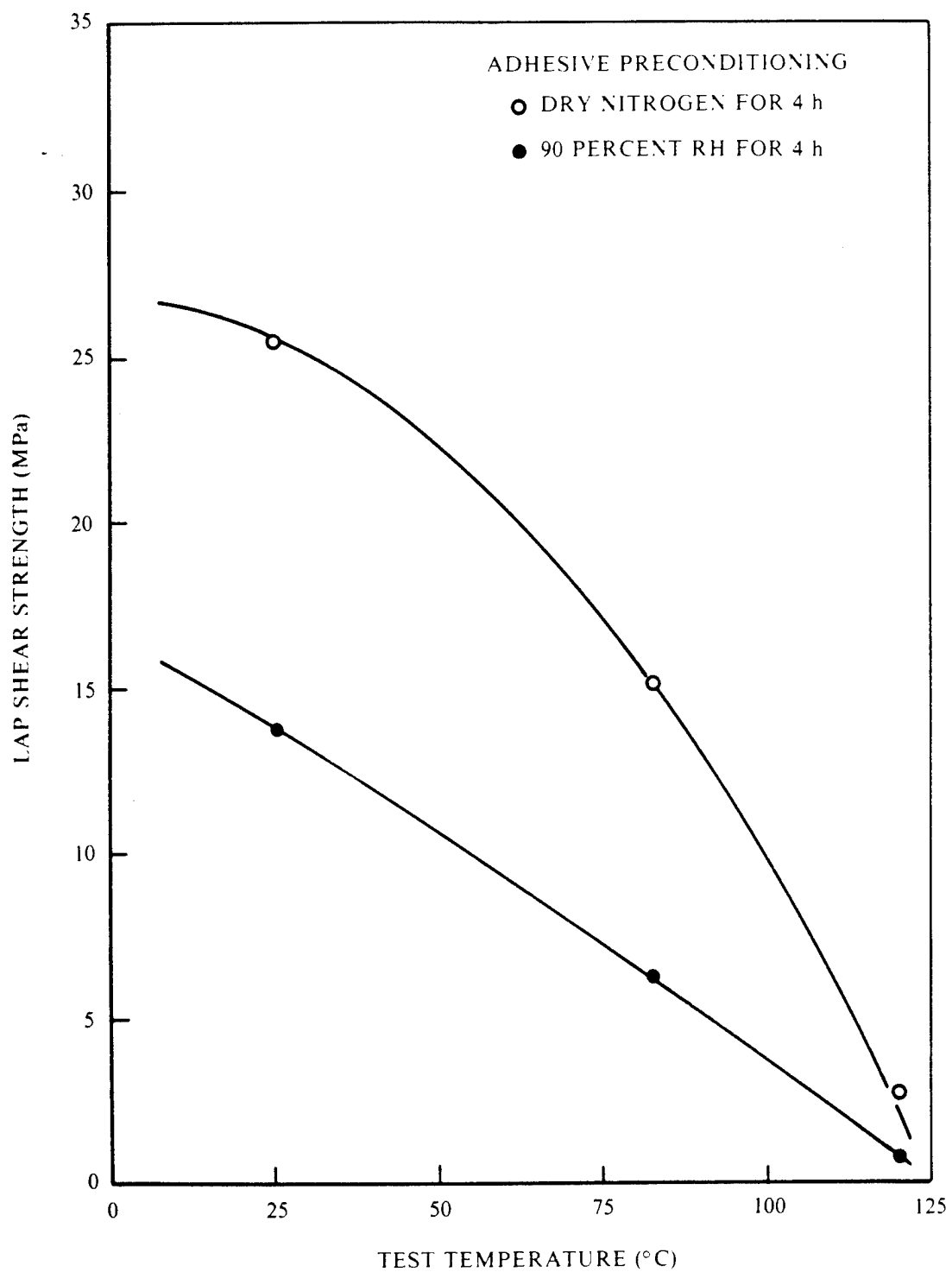


Figure 5. Elevated Temperature Lap Shear Strength

Table 4. Outgassing Results

Temperature Range (°C)	Outgassing Products
30 to 35	Intense diluent--butyl glycidyl ether. Trace of water.
35 to 50	Intense diglycidyl ether of Bisphenol-A (DGEBA). Minor--butyl glycidyl ether diluent.
50 to 65	Same products as in the 35° to 50°C range, but decreasing diluent intensity.
65 to 75	Intense--DGEBA. Minor--dicyandiamide. Trace--butyl glycidyl ether diluent.
85 to 100	Intense--DGEBA. Minor--secondary amine. Trace--toluene amine.
100 to 120	Intense--DGEBA. Minor--dicyandiamide (increasing in intensity).

When the mechanical test specimens (lap shear, T-Peel) were prepared and the adhesive preconditioned, it was not known that the FM-123-5 contained the reactive diluent butyl glycidyl ether. Therefore, the adhesive should not be preconditioned in flowing dry nitrogen or especially in vacuum for any length of time because of possible removal of the diluent. Preconditioning only in a desiccator to remove moisture is recommended (Figure 3).

ACCOMPLISHMENTS

The results and test data showed the following.

1. An acceptable cure can be achieved at 85°C; however, a cure time of 8 hours is strongly recommended to ensure a sufficiently high (>90°C) Tg. A high temperature cure (116°C) with high pressure (0.21 MPa) will provide the highest strength results.
2. The adhesive will absorb moisture that can affect the Tg and strength of the cured adhesive. Of the two preconditioning methods evaluated--flowing dry nitrogen and desiccated storage for 30 minutes--the latter produces the better results. When the adhesive is removed from the freezer, the

polyethylene covers should be left on both sides until use. This action reduces loss of any residual solvent or diluent and reduces surface area for moisture to condense. It also minimizes possible contamination. The assembly is fabricated in a controlled environment (maximum temperature of 25°C and RH of ≤15 percent), which is an acceptable procedure.

3. Preconditioning is needed to remove moisture for adhesive bonds which will eventually experience elevated temperatures. Curing at optimum temperature, pressure, and time is necessary to achieve maximum strength for elevated temperature application.

FUTURE WORK

To verify the degree of cure of the adhesive bond, a sample of the adhesive should be cured along with the product. The sample should be tested on a TMA to verify that a sufficiently high (≥90°C) Tg has been obtained.

REFERENCE

¹"FM-123-5 Adhesive Film," (Revised), American Cyanamid Company, Bloomingdale Department, April 8, 1969.

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SPECIAL PROJECTS: Adhesive Curing

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